Supporting Information

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Guest Covalent Capture by a Host: A Biomimetic Strategy for the Selective Functionalization of a Cavity

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chem_201202391_sm_miscellaneous_information.pdf
Supporting Information


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Safety Note. Caution! Although we have not encountered any problems, it is noted that perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions. Identically, organic azides are potentially explosive and should be manipulated carefully. For those reasons, the complexes were not dried using elevated temperature and they can still contain some small amounts of solvent used during the synthesis as it is observed by $^1$H NMR spectroscopy.

Solvents CH$_3$CN and CH$_2$Cl$_2$ were dried over CaH$_2$ and distilled. THF was dried over sodium and distilled. Other solvents and chemicals were of reagent grade and were used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a Brucker ARX (250 MHz) spectrometer or an Advance 500 spectrometer (500 MHz). MS (ESI) analyses were obtained with a ThermoFinnigen LCQ Advantage spectrometer using methanol, dichloromethane or acetonitrile as solvents. HRMS were performed at the Institut de Chimie des Substances Naturelles, France. IR spectra were obtained with a Perkin-Elmer Spectrum on FTIR spectrometer equipped with a MIRacleTM single reflection horizontal ATR unit (germanium crystal).

1. Synthesis of the acetylenic guests.

1.1 Alcohols

a. 4-Pentyn-1-ol and 5-Hexyn-1-ol

4-Pentyn-1-ol and 5-hexyn-1-ol were purchased from Sigma Aldrich and were used without purification.

b. 6-(4-methoxyphenyl)-5-hexyn-1-ol

6-(4-methoxyphenyl)5-hexyn-1-ol was synthesized according to a reported procedure.


c. 6-(4-nitrophenyl)-5-hexyn-1-ol

6-(4-nitrophenyl)-5-hexyn-1-ol was synthesized according to a reported procedure.


d. 3-ethylbenzyl alcohol

3-Ethynylbenzyl alcohol was synthesized according to a reported procedure.

1.2 Amines

a. 4-Pentyn-1-amine

4-Pentyn-1-amine was synthesized according to a described procedure.


b. 5-Hexyn-1-amine

5-Hexyn-1-amine was synthesized according to a described procedure.


c. 6-Heptyn-1-amine

6-Heptyn-1-amine was synthesized according to a described procedure.


d. 3-Ethynylbenzylamine

3-ethynylbenzylamine was synthesized according to a described procedure.


e. 6-(4-methoxyphenyl)-5-hexyn-1-amine and 6-(nitrophenyl)-5-hexyn-1-amine

Both amines were synthesized in three steps from the corresponding alcohols.

• Mesylation

**General Procedure:** Triethylamine (152 µL, 1.10 mmol, 1.2 eq) was added dropwise at 0°C under argon to a solution of the appropriate alcohol (0.91 mmol, 1.0 eq) and mesyl chloride (85 µL, 1.10 mmol, 1.2 eq) in freshly distilled dichloromethane (5 mL). The mixture was stirred at 0°C for 5 minutes then for 1 hour at room temperature. The reaction was quenched with a saturated NaHCO₃ solution (10 mL). The mesylate was extracted with dichloromethane (2x 10 mL) and the combined organic layers were washed with NaHCO₃ (2x 10 mL) and water (1x 10 mL), dried over MgSO₄ and concentrated under reduced pressure to provide the corresponding mesylate, which was used without further purification.

6-(4-nitrophenyl)-5-hexyn-1-methylsulfonate

![Image of 6-(4-nitrophenyl)-5-hexyn-1-methylsulfonate structure]
Reddish oil, 95 % yield.

$^1$H NMR (500 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 1.64 (m, 2H, c), 1.82 (m, 2H, b), 2.40 (t, $J = 6.9$ Hz, 2H, d), 2.93 (s, 3H, CH$_3$), 4.19 (t, $J = 6.3$ Hz, 2H, a), 7.37 (d, $J = 8.5$ Hz, 2H, ArH), 7.99 (d, $J = 8.5$ Hz, 2H, ArH). $^{13}$C NMR (125 MHz, CDCl$_3$, 300 K) $\delta$ (ppm): 14.66 (c), 18.63 (b), 24.01 (d), 36.83 (CH$_3$), 66.43 (a), 79.57 (f), 95.26 (e), 123.14 (i), 130.49 (g), 131.99 (h), 146.32 (j). IR $\nu$ (cm$^{-1}$): 749.4, 853.2, 971.8, 1011.4, 1107.7, 1172.0 (strong, OMs stretch), 1342.5 (strong, NO$_2$ sym. stretch), 1515.5 (medium, NO$_2$ asym str.), 1592.2, 2228.2 (w, alkyne str).

Figure S1.1 $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) of 6-(4-nitrophenyl)-5-hexyn-1-methylsulfonate.

Figure S1.2 $^{13}$C NMR (CDCl$_3$, 125 MHz, 300 K) of 6-(4-nitrophenyl)-5-hexyn-1-methylsulfonate.

6-(4-methoxyphenyl)-5-hexyn-1-methylsulfonate

Yellow oil, 98 % yield.

$^1$H NMR (250 MHz, 300 K, CDCl$_3$) $\delta$ (ppm): 1.72 (m, 2H, c), 1.95 (m, 2H, b), 2.47 (t, $J = 6.8$ Hz, d), 2.98 (s, 3H, SCH$_3$), 3.80 (s, 3H, OCH$_3$), 4.30 (t, $J = 6.3$ Hz, a), 6.81 (d, $J = 8.8$ Hz), 7.32 (d, $J = 8.8$ Hz).
$^1$H NMR (CDCl$_3$, 250 MHz, 300 K) of 6-(4-methoxyphenyl)-5-hexyn-1-methylsulfonate.

$^{13}$C NMR (CDCl$_3$, 63 MHz, 300 K) of 6-(4-methoxyphenyl)-5-hexyn-1-methylsulfonate.

- **Azides**

**General procedure:** A solution of the corresponding mesylate (0.96 mmol, 1.0 eq) and sodium azide (94 mg, 1.44 mmol, 1.5 eq) in DMF (5mL) was heated at 50°C for 3 hours. The azide was extracted with ether (2x 10 mL) and the combined organic layers were washed with water (5x 10 mL), dried over MgSO$_4$ and evaporated.
6-(4-nitrophenyl)-5-hexyn-1-azide

Reddish oil, 85 %.

\(^1\)H NMR (500 MHz, 300 K, CDCl\(_3\)) \(\delta\) (ppm): 1.70 (m, 2H, c), 1.76 (m, 2H, b), 2.48 (t, \(J = 6.6\) Hz, 2H, d), 3.33 (t, \(J = 6.5\) Hz, 2H, a), 7.47 (d, \(J = 8.5\) Hz, 2H, ArH), 8.11 (d, \(J = 8.5\) Hz, 2H, ArH). \(^{13}\)C NMR (125 MHz, 300K, CDCl\(_3\)) \(\delta\) (ppm): 19.17 (c), 25.54 (b), 28.07 (d), 50.95 (a), 79.86 (f), 95.55 (e), 123.47 (i), 130.86 (g), 132.28 (h), 146.72 (j). IR \(\nu\) (cm\(^{-1}\)): 712.3, 759.3, 798.8, 853.2, 1006.4, 1102.8, 1253.5, 1327.7, 1503.2, 1594.6, 2096.2 (N\(_3\), stretch), 2862.7.

**Figure S1.5** \(^1\)H NMR (CDCl\(_3\), 500 MHz, 300 K) of 6-(4-nitrophenyl)-5-hexyn-1-azide.

**Figure S1.6** \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, 300 K) of 6-(4-nitrophenyl)-5-hexyn-1-azide.
6-(4-methoxyphenyl)-5-hexyn-1-azide

Yellow oil, 81%.

\(^1\)H NMR (500 MHz, 300 K, CDCl\(_3\)) \(\delta\) (ppm): 1.67 (m, 2H, c), 1.77 (m, 2H, b), 2.43 (t, \(J = 6.7\) Hz, 2H, d), 3.31 (t, \(J = 6.7\) Hz, 2H, a), 3.77 (s, 3H, OCH\(_3\)), 6.81 (d, \(J = 8.8\) Hz, 2H, ArH), 7.33 (d, \(J = 8.8\) Hz, 2H, ArH). \(^13\)C NMR (125 MHz, 300K, CDCl\(_3\)) \(\delta\) (ppm): 18.96 (c), 25.90 (b), 28.02 (d), 51.00 (a), 55.16 (k), 80.98 (OCH\(_3\)), 87.62 (e), 113.84 (i), 115.96 (g), 132.84 (h), 159.15 (j). IR ν (cm\(^{-1}\)): 830.9, 1031.1, 1088.0, 1105.3, 1172.0, 1243.7, 1288.2, 1461.2, 1508.1, 1508.1, 1607.0, 1678.7, 2094.2 (N\(_3\), stretch), 2937.9.

![Figure S1.7 \(^1\)H NMR (CDCl\(_3\), 500 MHz, 300 K) of 6-(4-methoxyphenyl)-5-hexyn-1-azide.](image-url)
Figure S1.8 $^{13}$C NMR (CDCl$_3$, 125 MHz, 300 K) of 6-(4-nitrophenyl)-5-hexyn-1-methylsulfonate.

- Reduction of the azide

6-(4-nitrophenyl)-5-hexyn-1-ammonium chloride

6-(4-nitrophenyl)-5-hexyn-1-azide (160 mg, 0.66 mmol, 1.0 eq) was dissolved in a 10:1 mixture of THF and water (10 mL). PPh$_3$ (206 mg, 0.79 mmol, 1.2 eq) was added and the mixture was stirred at room temperature overnight. HCl 37 % (3 mL) was added to the solution and THF was evaporated under reduced pressure. The residue was dissolved in dichloromethane (15 mL) and water (15 mL). The ammonium was extracted with 1M HCl (2x 10 mL) and the aqueous phase was washed with dichloromethane (2x 10 mL) and evaporated under reduced pressure to provide the hydrochloride as a yellow powder (126 mg, 0.50 mmol, 75 %). $^1$H NMR (500 MHz, 300 K, CD$_3$OD) δ (ppm): 1.70 (m, c), 1.86 (m, 2H, b), 2.53 (t, $J = 7.3$ Hz, 2H, d), 2.99 (t, $J = 7.6$ Hz, 2H, a), 7.53 (d, $J = 8.6$ Hz, 2H, ArH), 8.12 (t, $J = 8.6$ Hz, 2H, ArH). $^{13}$C NMR (125 MHz, 300 K, CD$_3$OD) δ (ppm): 19.64 (c), 23.32 (b), 27.72 (d), 40.36 (a), 80.76 (f), 96.08 (e), 124.49 (i), 131.99 (g), 133.45 (h), 148.06 (j). ESI-MS (CH$_3$OH) m/z: 219.1 (calc. 219.1 for [RNH$_3$]$^+$).

Figure S1.9 $^1$H NMR (CD$_3$OD, 500 MHz, 300 K) of 6-(4-nitrophenyl)-5-hexyn-1-ammonium chloride.
Figure S1.10 $^{13}$C NMR (CD$_3$OD, 125 MHz, 300 K) of 6-(4-nitrophenyl)-5-hexyn-1-ammonium chloride.

6-(4-methoxyphenyl)-5-hexyn-1-amine

6-(4-methoxyphenyl)-5-hexyn-1-azide (200 mg, 0.87 mmol, 1.0 eq) was dissolved in a 10:1 mixture of THF and water (10 mL). PPh$_3$ (229 mg, 0.79 mmol, 1.2 eq) was added and the mixture was stirred at room temperature overnight. HCl 37 % (4 mL) was added to the solution and THF was evaporated under reduced pressure. The residue was dissolved in dichloromethane (15 mL) and water (15 mL). The ammonium was extracted with 1M HCl (2x 10 mL) and the aqueous phase was washed with dichloromethane (2x 10 mL), then acidified to pH = 1 with HCl 37 %. The aqueous phase was then extracted with dichloromethane (2x 15 mL). The combined organic layers were dried over anhydrous sodium sulfate and evaporated under reduced pressure to provide 6-(4-methoxyphenyl)hex-5-yn-1-amine as a white solid (133 mg, 0.66 mmol, 75 %). $^1$H NMR (500 MHz, 300 K, CDCl$_3$) $\delta$ (ppm): 1.63 (m, 4H, b+c), 2.41 (t, $J$ = 6.7 Hz, 2H, d), 2.75 (m, 2H, a), 3.79 (s, 3H, OCH$_3$), 6.80 (d, $J$ = 8.0 Hz, 2H, ArH), 7.32 (d, $J$ = 8.0 Hz, 2H, ArH). $^{13}$C NMR (63 MHz, 300K, CDCl$_3$) $\delta$ (ppm): 19.0 (c), 25.9 (b), 32.8 (d), 41.5 (a), 54.8 (k), 80.3 (f), 88.1 (e), 113.5 (i), 115.8 (g), 132.5 (h), 158.7 (j). IR $\nu$ (cm$^{-1}$): 798.7, 1026.1, 1090.1, 1172.0, 1259.3, 1289.0, 1376.5, 1461.2, 1508.6, 1605.4, 2852.2, 2918.1. ESI-MS (CH$_3$OH) $m/z$: 204.1 (calcd. 204.1 for [M+H]$^+$).
Figure S1.11 $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) of 6-(4-methoxyphenyl)-5-hexyn-1-amine.

Figure S1.12 $^{13}$C NMR (CDCl$_3$, 63 MHz, 300 K) of 6-(4-methoxyphenyl)-5-hexyn-1-amine.
2. General procedure for the monoclick reaction with amines

Precursor complex [Zn.X₆N₃](ClO₄)₂ (200 mg, 0.13 mmol, 1.0 eq) was added to a solution of the appropriate amine (ca. 3 eq) in dry toluene (10 mL). The resulting mixture was refluxed under argon for two hours (for C₃NH₂ and C₄NH₂) and five hours (for C₅NH₂). Toluene was evaporated under reduced pressure and the residue was taken in a minimum volume of acetonitrile (ca. 3 mL). The calixarene is then precipitated with ether (30 mL). The solid is filtered, washed with ether (3x 10 mL) and dried under vacuum.

3. General procedure for the monoclick reaction with alcohols

Precursor complex [Zn.X₆N₃](ClO₄)₂ (200 mg, 0.13 mmol, 1.0 eq) was added to a solution of the appropriate alcohol (10 eq) in dry toluene (10 mL). The resulting mixture was refluxed under argon for four hours. Toluene was evaporated under reduced pressure and the residue was taken in a minimum volume of acetonitrile (ca. 3 mL). The calixarene is then precipitated with ether (30 mL). The solid is filtered, washed with ether (3x 10 mL) and dried under vacuum. In the case of 6-(4-nitrophenyl)-5-hexyn-1-ol, the pure monofunctionalized complex was obtained without further purification. In the case of 5-hexyn-1-ol, 4-pentyn-1-ol and 3-ethynylbenzyl alcohol, the crude product was purified by column chromatography on basic alumina (CH₂Cl₂/CH₃OH/NH₃(27%) 99:1:0.01) to obtain the pure monofunctionalized calixarene ligand.

Recomplexation step

The monofunctionalized ligand (20 mg, 1.0 eq) is dissolved in a 1:1 mixture of CH₂Cl₂ and CH₃CN (1 mL). A solution of zinc perchlorate hexahydrate in a minimum amount of THF (1.0 eq) is added to the solution of ligand. After stirring for 15 min, ether is added (10 mL). The resulting precipitate is filtered and dried under vacuum to provide the corresponding Zn(II) complex as a white solid in 94-98 % yield.

4.1 [Zn_{C3NH2}](ClO_4)_2

White solid, 95 %.

The spectroscopic data for complex [Zn_{C3NH2}](ClO_4)_2 was identical to its previous description (B. Colasson, O. Reinaud J. Am. Chem. Soc. 2008, 130, 15226-15227).

4.2 [Zn_{C4NH2}](ClO_4)_2

White solid, 93 %.

^1H (500 MHz, CD_3CN, 300 K) δ (ppm): -1.09 (m, 2H, β), -0.25 (m, 2H, γ), 0.78 (m, 2H, α), 1.34 (s, 18H, 'Bu), 1.41 (s, 9H, 'Bu), 1.57 (t, 7.5Hz, 2H, δ), 2.20 (m, 2H, NH_2), 3.48 (d, J = 14 Hz, 2H, ArCH_2), 3.53 (d, J = 14 Hz, 2H, ArCH_2), 3.57 (s, 6H, OCH_3), 3.69 (d, J = 14 Hz, 2H, ArCH_2), 3.76 (s, 3H, OCH_3), 3.77 (s, 6H, NCH_3), 3.81 (s, 3H, NCH_3), 4.10 (br m, 6H, ArCH_2), 5.18 (d, J =14.8 Hz, 2H, ImCH_2), 5.28 (d, J = 14.8 Hz, 2H, ImCH_2), 5.38 (s, 2H, ImCH_2), 6.10 (s, 2H, HArN_3), 6.24 (s, 2H, HArN_3), 6.28 (s, 2H, HAr_tria), 6.87 (s, 1H, ImH), 6.90 (s, 2H, ImH), 7.24 (s, 1H, H_tria), 7.45 (m, 6H, HAr_{Bu} + ImH). ^13C (125 MHz, CD_3CN, 300 K) δ (ppm): 21.9 (δ), 25.2 (γ), 30.7 (ArCH_2), 31.3 (β), 31.5 (ArCH_2), 32.1 (‘Bu), 32.2 (‘Bu), 35.5 (NCH_3), 35.7 (NCH_3), 41.5 (α), 61.7 (OCH_3), 62.1 (OCH_3), 66.1 (ImCH_2), 66.2 (ImCH_2), 118.2, 124.4, 125.4, 125.5, 128.8, 130.5, 130.7, 130.8, 132.9, 133.2, 133.5, 136.5, 137.0, 137.1, 137.2, 138.7, 147.8, 149.8, 149.9, 153.0, 155.3, 155.5, 156.5. IR ν (cm⁻¹): 761.7, 818.6, 868.0, 976.8, 999.0, 1097.9 (s, ClO_4⁻), 1162.1, 1186.8, 1199.2, 1233.8, 1293.1, 1325.2, 1362.3, 1461.2, 1478.5, 1503.2, 1594.6, 1611.9, 2109.1 (N_tria, stretch), 2957.8 (CH, stretch). **ESI-MS**
(CH₃OH) m/z: 1511.6 (calc. 1511.6 for [ZnM₄NH₂⁺ClO₄]⁺) HRMS after demetallation m/z: 1349.7516 for [M₄NH₂⁺H]⁺ (calc 1349.7464).

Figure S4.1 ¹H NMR (CD₃CN, 500 MHz, 300 K) of [ZnM₄NH₂](ClO₄)₂

Figure S4.2 ¹³C NMR (CD₃CN, 125 MHz, 300 K) of [ZnM₄NH₂](ClO₄)₂
Figure S4.3 COSY NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnM$_{4}$NH$_2$](ClO$_4$)$_2$

Figure S4.4 HSQC NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnM$_{4}$NH$_2$](ClO$_4$)$_2$
Figure S4.5 ESI-MS (positive ionization, CH$_3$OH) of ligand M$_{C4NH2}$, displaying peaks for [M$_{C4NH2}$+H]$^+$ (1349.6), [M$_{C4NH2}$+Na]$^+$ (1371.6) and [M$_{C4NH2}$+2H]$^{2+}$ (675.3).

Figure S4.6 $^1$H NMR of monofunctionalized complex [ZnM$_{C4NH2}$]$^{2+}$ (CDCl$_3$, 500 MHz) between 330 K and 264 K. (S: residual solvent).
4.3 \([\text{ZnM}_{5}\text{NH}_2](\text{ClO}_4)_2\)

White solid, 92%.

\(^1\text{H} (500 \text{ MHz, } \text{CD}_3\text{CN, 353 K}) \delta (\text{ppm}): -1.00 (\text{m, 2H, } \beta), -0.60 (\text{m, 2H, } \gamma), 0.68 (\text{m, 2H, } \delta), 0.83 (\text{m, 2H, } \alpha), 1.40 (\text{s, 18H, } \text{'Bu}), 1.44 (\text{s, 9H, } \text{'Bu}), 2.09 (\text{t, 7.6Hz, 2H, } \varepsilon), 2.61 (\text{m, 2H, NH}_2), 3.48 (\text{d, } J = 14 \text{ Hz, 2H, ArCH}_2), 3.57 (\text{d, } J = 14 \text{ Hz, 4H, ArCH}_2), 3.67 (\text{s, 6H, OCH}_3), 3.76 (\text{s, 3H, OCH}_3), 3.77 (\text{s, 6H, NCH}_3), 3.81 (\text{s, 3H, NCH}_3), 4.15 (\text{d, } J = 14 \text{ Hz, 4H, ArCH}_2), 4.25 (\text{d, } J = 14 \text{ Hz, 2H, ArCH}_2), 5.35 (\text{d, } J = 14.8 \text{ Hz, 2H, ImCH}_2), 5.37 (\text{s, 2H, ImCH}_2), 5.42 (\text{s, 2H, ImCH}_2), 6.16 (\text{s, 2H, HArN}_3), 6.18 (\text{s, 1H, HArN}_3), 6.70 (\text{s, 2H, HAr}_{\text{nu}}, 6.90 (\text{s, 2H, ImH}), 6.98 (\text{s, 2H, ImH}), 7.28 (\text{s, 1H, H}_{\text{nu}}), 7.44 (\text{d, } J = 2.5 \text{ Hz, 2H, HAr}_{\text{beta}}), 7.46 (\text{s, 2H, HAr}_{\text{beta}}), 7.49 (\text{d, } J = 2.5 \text{ Hz, 2H, HAr}_{\text{beta}}), 7.50 (\text{d, } J = 1.6 \text{ Hz, 1H, ImH}), 7.53 (\text{d, } J = 1.6 \text{ Hz, 2H, ImH}). \ ^{13}\text{C} (125 \text{ MHz, } \text{CD}_3\text{CN, 300 K}) \delta (\text{ppm}): \text{IR } \nu (\text{cm}^{-1}): 751.6, 807.3, 1001.5, 1103.4, 1185.7, 1201.2, 1241.2, 1290.6, 1364.8, 1453.8, 1479.6, 1594.2, 2108.4, 2961.9. \text{ESI-MS (CH}_3\text{OH) } m/z: 1525.6 (\text{calc. 1525.6 for [ZnM}_{5}\text{NH}_2\text{+ClO}_4^-}) \text{ HRMS after demetallation } m/z: 1363.6580 \text{ for [M}_{5}\text{NH}_2\text{+H}^+] (\text{calc 1363.6620}).
Figure S4.7 $^1$H NMR (CD$_3$CN, 500 MHz, 353 K) of [ZnM(C$_5$NH$_2$)](ClO$_4$)$_2$

Figure S4.8 COSY NMR (CD$_3$CN, 500 MHz, 353 K) of [ZnM(C$_5$NH$_2$)](ClO$_4$)$_2$
Figure S4.9 HSQC NMR (CD$_3$CN, 500 MHz, 353 K) of [ZnM$_{5}$N$_{2}$](ClO$_{4}$)$_{2}$

Figure S4.10 ESI-MS (positive ionization, CH$_3$OH) of ligand M$_{5}$N$_{2}$, displaying peaks for [M$_{5}$N$_{2}$+H]$^+$ (1363.6), [M$_{5}$N$_{2}$+Na]$^+$ (1385.7), [M$_{5}$N$_{2}$+2H]$^{2+}$ (682.4) and [M$_{5}$N$_{2}$+3H]$^{3+}$ (455.2).
Figure S4.11 $^1$H NMR of monofunctionalized complex [ZnM$_{5}$N$_{2}$H$_{2}$]$^{2+}$ (CD$_3$CN, 500 MHz) between 330 K and 264 K. (S: residual solvent).

4.4 [ZnM$_{ArCH_{2}NH_{2}}$](ClO$_4$)$_2$

White solid, 95 %.

$^1$H (500 MHz, CD$_3$CN, 300 K) δ (ppm): 1.27 (s, 18H, 'Bu), 1.45 (s, 9H, 'Bu), 2.38 (m, 1H, NH), 2.58 (m, 1H, NH), 3.39 (d, $J = 15.7$ Hz, 2H, ArCH$_2$), 3.53 (s, 3H, OCH$_3$), 3.63 (d, $J = 15.7$ Hz, 2H, ArCH$_2$), 3.70 (d, $J = 15.7$ Hz, 2H, ArCH$_2$), 3.78 (s, 6H, OCH$_3$), 3.78 (s, 3H, NCH$_3$), 3.91 (s, 3H, NCH$_3$), 3.92 (d, $J = 15.7$ Hz, ArCH$_2$), 4.22 (d, $J = 15.7$ Hz, 2H, ArCH$_2$), 4.31 (d, $J=15.7$Hz, 2H, ArCH$_2$), 4.67 (d, $J = 7.7$ Hz, 1H, a), 4.94 (s, 1H, d), 5.27 (s, 4H, ImCH$_2$), 5.59 (s, 2H, ImCH$_2$), 5.67 (s, 2H, HArN$_3$), 6.21 (s, 2H, HArN$_3$), 6.43 (s, 2H, HAr$_{tra}$), 6.48 (t, $J = 7.7$ Hz, 1H, b), 6.90 (s, 1H, ImH), 6.98 (s, 2H,
ImH), 7.20 (d, J = 7.7 Hz, 1H, c), 7.27 (d, J = 2.2 Hz, 2H, HAr_tBu), 7.38 (d, J = 2.2 Hz, 2H, HAr_tBu), 7.51 (s, 1H, ImH), 7.52 (d, J = 2.2 Hz, 2H, HAr_tBu), 7.56 (s, 2H, ImH), 7.80 (s, 1H, Htria). $^{13}$C (125 MHz, CD$_3$CN, 300 K) δ (ppm): 30.4 (ArCH$_2$), 31.2 (ArCH$_2$), 32.0 (tBu), 32.2 (tBu), 35.4 (NCH$_3$), 35.8 (NCH$_3$), 44.38 (CH$_2$NH$_2$), 61.1 (OCH$_3$), 61.2 (OCH$_3$), 66.2 (ImCH$_2$), 117.30, 119.03, 124.46, 125.01, 125.24, 126.09, 126.20, 126.62, 128.00, 128.55, 129.84, 130.08, 130.46, 130.59, 131.64, 131.72, 132.45, 132.73, 134.32, 134.96, 135.92, 136.37, 137.17, 137.88, 139.28, 147.33, 147.54, 149.21, 149.66, 152.11, 154.72, 154.91, 157.06. IR ν (cm$^{-1}$): 761.7, 796.3, 870.5, 996.5, 1097.9 (s, ClO$_4^-$), 1189.3, 1236.3, 1290.6, 1325.2, 1362.3, 1436.5, 1458.7, 1478.5, 1503.2, 1597.1, 2104.2 (N$_3$, stretch), 2957.8, 3493.7 (br). ESI-MS (CH$_3$OH) m/z: 1545.6 (calc. 1545.6 for [ZnMArCH$_2$NH$_2$+ClO$_4$]$^+$) HRMS m/z: 1383.7371 for [MArCH$_2$NH$_2$+H]$^+$ (calc 1383.7307).

Figure S4.12 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnMArCH$_2$NH$_2$](ClO$_4$)$_2$
Figure S4.13 $^{13}$C NMR (CD$_3$CN, 125 MHz, 300 K) of [ZnMe$_2$(CH$_2$NH$_2$)(ClO$_4$)$_2$]

Figure S4.14 HSQC NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnMe$_2$(CH$_2$NH$_2$)(ClO$_4$)$_2$]
Figure S4.15 COSY NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnM$_{ArCH2NH2}$](ClO$_4$)$_2$

Figure S4.16 ESI-MS (positive ionization, CH$_3$OH) of ligand M$_{ArCH2NH2}$, displaying peaks for [M$_{ArCH2NH2}$+H]$^+$ (1383.5), [M$_{ArCH2NH2}$+Na]$^+$ (1405.4), [M$_{ArCH2NH2}$+2H]$^{2+}$ (692.3) and [M$_{ArCH2NH2}$+3H]$^{3+}$ (461.9).
White solid, 91%.

$^1$H (500 MHz, CD$_3$CN, 300 K) δ (ppm): -1.10 (m, 2H, β), -0.17 (m, 2H, γ), 0.83 (m, 2H, α), 1.34 (s, 18H, tBu), 1.40 (s, 9H, tBu), 1.76 (t, J = 7.0 Hz, 2H, δ), 2.23 (m, 2H, NH$_2$), 3.50 (d, J = 15.5 Hz, 2H, ArCH$_2$), 3.56 (d, J = 15.5 Hz, 2H, ArCH$_2$), 3.59 (s, 6H, OCH$_3$), 3.71 (d, J = 15.5 Hz, 2H, ArCH$_2$), 3.78 (s, 6H, NCH$_3$), 3.79 (s, 3H, OCH$_3$), 3.83 (s, 3H, NCH$_3$), 4.09 (br s, 6H, ArCH$_2$), 5.18 (d, J = 14.5 Hz, 2H, ImCH$_2$), 5.29 (d, J = 14.5 Hz, 2H, ImCH$_2$), 5.39 (s, 2H, ImCH$_2$), 6.05 (s, 2H, HArN$_3$), 6.26 (s, 2H, HArN$_3$), 6.34 (s, 2H, HAr$_{tBu}$), 6.91 (s, 1H, ImH), 6.95 (s, 2H, ImH), 7.41 (s, 4H, HAr$_{tBu}$), 7.51 (s, 3H, ImH), 7.68 (d, J = 8.5 Hz, 2H, HArNO$_2$), 8.17 (d, J = 8.5 Hz, 2H, HArNO$_2$).

$^{13}$C (125 MHz, CD$_3$CN, 300 K) δ (ppm): 21.6 (γ), 23.9 (δ), 30.1 (β), 31.2, 31.4, 31.7, 35.1 (NCH$_3$), 35.3 (NCH$_3$), 40.7 (α), 61.3 (OCH$_3$), 61.7 (OCH$_3$), 65.6 (ImCH$_2$), 65.8 (ImCH$_2$), 124.98, 125.17, 127.77, 128.40, 128.47, 130.18, 130.29, 130.52, 132.50, 136.09, 136.27, 136.45, 136.77, 136.95, 138.91, 142.13, 147.41, 148.01, 149.46, 149.54, 152.69, 154.80, 154.95, 156.40. IR ν (cm$^{-1}$): 759.3, 853.2, 974.3, 1001.5, 1100.3 (ClO$_4$-), 1159.6, 1199.2, 1233.8, 1290.6, 1340.1 (NO$_2$ symmetric stretch), 1458.7, 1478.5, 1503.2, 1518.0 (NO$_2$ antisymmetric stretch), 1597.1, 2104.2 (N$_3$ stretch), 2957.8 (CH stretch).

ESI-MS (CH$_3$OH) m/z: 1632.6 (calc. 1632.6 for [ZnM$_6$NO$_2$ArC$_4$NH$_2$ClO$_4$]$^+$) HRMS after demetallation m/z: 1470.7690 for [M$_6$NO$_2$ArC$_4$NH$_2$+H]$^+$ (calc 1470.7628).
Figure S4.17 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnM$_{p}$NO$_2$ArC$_4$NH$_2$](ClO$_4$)$_2$

Figure S4.18 $^{13}$C NMR (CD$_3$CN, 125 MHz, 300 K) of [ZnM$_{p}$NO$_2$ArC$_4$NH$_2$](ClO$_4$)$_2$
Figure S4.19 ESI-MS (positive ionization, CH$_3$OH) of ligand M$_{pNO2ArC4NH2}$, displaying peaks for [M$_{pNO2ArC4NH2}$H]$^+$ (1470.6, cf. Figure 4.18 for zoom), [M$_{pNO2ArC4NH2}$Na]$^+$ (1492.5), [M$_{pNO2ArC4NH2}$2H]$^{2+}$ (736.3).

Figure S4.20 ESI-MS (positive ionization, CH$_3$OH) of ligand M$_{pNO2ArC4NH2}$. Zoom on the [M$_{pNO2ArC4NH2}$H]$^+$ peak (1470.6).
White powder, 92 %.

$^1$H (500 MHz, CD$_3$CN, 300 K) δ (ppm): -1.12 (m, 2H, $\beta$), -0.22 (m, 2H, $\gamma$), 0.82 (m, 2H, $\alpha$), 1.35 (s, 18H, $t$Bu), 1.40 (s, 9H, $t$Bu), 1.69 (t, $J = 7.0$ Hz, 2H, $\delta$), 2.21 (m, 2H, NH$_2$), 3.50 (d, $J = 15.5$ Hz, 2H, ArCH$_2$), 3.55 (d, $J = 15.5$ Hz, 2H, ArCH$_2$), 3.57 (s, 6H, OCH$_3$), 3.70 (d, $J = 15.7$ Hz, 2H, ArCH$_2$), 3.76 (s, 3H, OCH$_3$), 3.77 (s, 6H, NCH$_3$), 3.81 (s, 3H, NCH$_3$), 4.08 (br s, 6H, ArCH$_2$), 5.17 (d, $J = 14$ Hz, 2H, ImCH$_2$), 5.29 (d, $J = 14$ Hz, 2H, ImCH$_2$), 5.37 (s, 2H, ImCH$_2$), 6.07 (s, 2H, HArN$_3$), 6.24 (s, 2H, HArN$_3$), 6.32 (s, 2H, HAr$_{tBu}$), 6.89 (s, 1H, ImH), 6.91 (d, $J = 8.7$ Hz, 2H, HArOCH$_3$), 6.93 (s, 2H, ImH), 7.36 (d, $J = 8.7$ Hz, 2H, HArOCH$_3$), 7.42 (s, 4H, HAr$_{tBu}$), 7.46 (s, 2H, HAr$_{tBu}$), 7.50 (s, 3H, ImH). $^{13}$C (125 MHz, CD$_3$CN, 300 K) δ (ppm): 21.82 ($\gamma$), 24.45 ($\delta$), 30.00 ($\beta$), 31.56 ($t$Bu), 32.08 ($t$Bu), 35.58 (NCH$_3$), 35.74 (NCH$_3$), 41.22 ($\alpha$), 61.70 (OCH$_3$), 62.1 (OCH$_3$), 66.0 (ImCH$_2$), 66.7 (ImCH$_2$), 115.4, 125.2, 125.4, 125.5, 128.8, 128.9, 129.3, 132.6, 133.4, 134.1, 134.4, 136.5, 136.8, 137.1, 144.6, 147.8, 149.9, 150.0, 153.0, 155.2, 155.4, 156.5. IR ν (cm$^{-1}$): 751.8, 839.0, 1001.5, 1083.0, 1244.8, 1288.2, 1362.3, 1438.9, 1478.1, 1508.1, 1599.6, 2106.6, 2950.0. ESI-MS (CH$_3$OH) m/z: 1617.6 (calc. 1617.7 for [ZnM$_5$Cl$_{12}$+ClO$_4$]$^+$) HRMS after demetallation m/z: 1455.7950 for [M$_{pOMeArC4NH2}$+H]$^+$ (calc 1455.7883).
Figure S4.21 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnM$_{pOMeArC4NH2}$](ClO$_4$)$_2$

Figure S4.22 $^{13}$C NMR (CD$_3$CN, 125 MHz, 300 K) of [ZnM$_{pOMeArC4NH2}$](ClO$_4$)$_2$
Figure S4.23 ESI-MS (positive ionization, CH₃OH) of ligand M_pOMeArC₄NH₂, displaying peaks for [M_pOMeArC₄NH₂+H]^+ (1455.5), [M_pOMeArC₄NH₂+Na]^+ (1478.5), [M_pOMeArC₄NH₂+2H]^{2+} (728.3) and [M_pOMeArC₄NH₂+3H]^+ (485.9).

4.7 M₄C₄OH et [ZnM₄C₄OH][(ClO₄)₂]

a. Ligand M₄C₄OH

Monofunctionalized calixarene was obtained as a free ligand after column chromatography on basic alumina.

Brown solid, 70-95 % depending on the run.

^1H (500 MHz, (CD₃)₂SO, 360 K) δ (ppm): 0.98 (s, 18H, 'Bu), 1.04 (s, 9H, 'Bu), 1.45 (m, 2H, γ), 1.65 (m, 2H, β), 2.70 (m, 2H, δ), 2.78 (br s, 3H, OCH₃), 2.98 (br s, 6H, OCH₃), 3.41 (t, J = 6.3 Hz, 2H, α), 3.55 (br s, 9H, NCH₃), 3.80 (br s, 12H, ArCH₂), 4.88 (s, 4H, ImCH₂), 4.98 (s, 2H, ImCH₂), 6.78 (br s, 6H, HArtBu), 6.82 (br s, 4H, HArN₃), 6.86 (s, 2H, ImH), 6.89 (s, 1H, ImH), 7.07 (br s, 3H, ImH), 7.31 (br s, 2H, HArtria), 7.64 (s, 1H, Htria). ^13C (125 MHz, CD₃CN, 300 K) δ (ppm): No spectrum
was recorded due to the broadness of the signals at 300 K. **HRMS** m/z: 1350.7362 for [M$_{4OH}$+H]$^+$ (calc. 1350.7304).

**Figure S4.24** $^1$H NMR (DMSO-d$_6$, 500 MHz, 360 K) of M$_{4OH}$

**Figure S4.25** COSY (DMSO-d$_6$, 500 MHz, 350 K) of M$_{4OH}$
Figure S4.26 HSQCmult (DMSO-d$_6$, 500 MHz, 350 K) of $\text{M}_{\text{C4OH}}$

Figure S4.27 ESI-MS (positive ionization, CH$_3$OH) of ligand $\text{M}_{\text{C4OH}}$, displaying peaks for $[\text{M}_{\text{C4OH}}^{+}\text{H}]^+$ (1350.7), $[\text{M}_{\text{C4OH}}^{+}\text{Na}]^+$ (1372.7), $[\text{M}_{\text{C5NH2}}^{+2}\text{H}]^{++}$ (675.8).
b. Complex \([\text{ZnM}_{4}\text{OH}]\)(\text{ClO}_4)_2

\(^1\text{H}\) (500 MHz, CD\(_3\)CN, 300 K) \(\delta\) (ppm): 1.33 (s, 18H, 'Bu), 1.38 (s, 9H, 'Bu), 1.48 (m, 4H, \(\beta+\gamma\)), 2.39 (t, \(J = 7.7\) Hz, 2H, \(\delta\)), 3.41 (t, \(J = 6.3\) Hz, 2H, \(\alpha\)), 3.54 (m, 2H, ArCH\(_2\)), 3.73 (s, 12H, OCH\(_3\)+NCH\(_3\)), 3.66 (s, 3H, OCH\(_3\)), 3.75 (s, 3H, NCH\(_3\)), 4.09 (br m, 6H, ArCH\(_2\)), 5.05 (s, 4H, ImCH\(_2\)), 5.08 (s, 2H, ImCH\(_2\)), 5.81 (s, 2H, HArN\(_3\)), 5.87 (s, 2H, HArN\(_3\)), 6.32 (s, 2H, HAr\(_{\text{mb}}\)), 6.89 (s, 1H, ImH), 6.92 (s, 2H, ImH), 7.36 (s, 1H, Htria), 7.41 (m, 9H, ImH+HAr\(_{\text{mb}}\)). \(^{13}\text{C}\) (125 MHz, CD\(_3\)CN, 300 K) \(\delta\) (ppm): 24.4 (\(\gamma\)), 25.6 (\(\beta\)), 31.6 ('Bu), 32.15 ('Bu), 33.0 (\(\delta\)), 35.4, 35.6, 61.5 (OCH\(_3\)), 62.3 (OCH\(_3\)), 65.2, 116.8, 117.0, 123.2, 125.4, 128.5, 130.3, 130.4, 132.7, 133.0, 133.3, 133.5, 136.4, 137.2, 137.3, 137.5, 139.2, 148.4, 149.3, 153.6, 155.7, 156.6. \(\text{IR }\nu\) (cm\(^{-1}\)): 759.3, 863.1, 929.8, 1001.5, 1100.3 (ClO\(_4\)), 1164.6, 1189.3, 1251.1, 1295.6, 1357.4, 1483.4, 1510.6, 1607.0, 2114.1, 2350.0, 2972.7. \(\text{ESI-MS}\) (CH\(_3\)OH) m/z: 1512.6 (calc. 1512.6 for \([\text{ZnM}_{4}\text{OH}]\)ClO\(_4\))

Figure S4.28 \(^1\text{H} \text{NMR} \) (CD\(_3\)CN, 500 MHz, 300 K) of \([\text{ZnM}_{4}\text{OH}]\)ClO\(_4\)\(_2\)

Figure S4.29 \(^1\text{H} \text{NMR} \) (CD\(_3\)CN, 500 MHz, 300 K) of \([\text{ZnM}_{4}\text{OH}]\)ClO\(_4\)\(_2\). Zoom on the high field region.
Figure S4.30 $^{13}$C NMR (CD$_3$CN, 125 MHz, 300 K) of [ZnM$_{40}$H](ClO$_4$)$_2$

Figure S4.31 $^1$H NMR (CD$_3$OD, 250 MHz, 300 K) of [ZnM$_{40}$H](ClO$_4$)$_2$
Figure S4.32 $^1$H NMR (CD$_3$OD, 250 MHz, 300 K) of [ZnM$_4$C$_4$OH]$_2$(ClO$_4$)$_2$. Zoom on the high-field region

c. Displacement of the self-coordinated hydroxyl chain.

Fig S4.31 represents the equilibrium of the displacement of the self-coordinated hydroxyl chain by an acetonitrile molecule, with the associated constant $K = [\text{out}]/[\text{in}]$. The relative proportions of the “in” and “out” complexes were determined by integration of the signals for methylenes $\beta$ and $\alpha$ respectively at various temperatures between 285 K and 340 K (Table S4.1). The associated van’t Hoff plot (Fig S4.32) gave the following thermodynamic parameters: $\Delta_r H^\circ = 1347 \times 8.31 = 11$ kJ.mol$^{-1}$ and $\Delta_r S^\circ = 7.11 \times 8.31 = 59$ J.K$^{-1}$.mol$^{-1}$.

![Chemical structure](image)

Figure S4.33 Displacement of the self-coordinated hydroxyl chain of [ZnM$_4$C$_4$OH]$_2^+$ by MeCN.

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<td>3.9</td>
<td>96.1</td>
<td>24.9</td>
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</table>

Table S4.1 Percentages of the “in” and “out” complexes of [ZnM$_4$C$_4$OH]$_2^+$ and associated equilibrium constant at various temperatures.
Figure S4.34 van’t Hoff plot associated with the displacement of the self-coordinated hydroxyl chain of [ZnM$_{40}$H]$_2^+$ by MeCN.

d. VT in CDCl$_3$

Figure S4.35 VT $^1$H NMR (CDCl$_3$, 500 MHz) of [ZnM$_{40}$H]$_2^+$. From bottom to top: 325 K, 310 K, 300 K, 265 K.
White powder, 82%.

$^1$H NMR (500 MHz, CD$_3$CN, 300 K) $\delta$ (ppm) : 1.35 (s, 18H, tBu), 1.38 (s, 9H, tBu), 1.60 (qt, $J$ = 7.1 Hz, 2H, $\beta$), 2.44 (t, $J$ = 7.2 Hz, 2H, $\gamma$), 3.41 (m, 2H, $\alpha$), 3.55 (m, 6H, ArCH$_{eq}$), 3.64 (s, 12H, OCH$_3$ + NCH$_3$), 3.66 (s, 3H, OCH$_3$), 3.76 (s, 3H, NCH$_3$), 4.07 (m, 6H, ArCH$_{eq}$), 5.04 (s, 4H, ImCH$_2$), 5.08 (s, 2H, ImCH$_2$), 5.82 (s, 2H, HAr$_{N3}$), 5.87 (s, 2H, HAr$_{N3}$), 6.34 (s, 2H, HAr$_{meta}$), 6.88 (s, 1H, ImH), 6.91 (s, 2H, ImH), 7.36 (s, 1H, H$_{tra}$), 7.38-7.44 (m, 9H, HAr$_{tBu}$ + ImH). $^{13}$C NMR (63 MHz, CD$_3$CN, 300 K) $\delta$ (ppm): 31.6, 32.1, 35.4, 35.6, 61.4, 61.5, 65.1, 101.4, 116.8, 117.0, 123.3, 125.3, 125.4, 128.5, 130.3, 130.4, 130.5, 132.7, 133.0, 136.5, 137.2, 137.3, 137.4, 148.4, 149.3, 149.4, 153.3, 155.5, 155.7, 156.6. IR (ATR) $\nu$ (cm$^{-1}$): 830.9, 1001.5, 1033.6, 1105.3, 1174.5, 1243.7, 1288.2, 1441.4, 1463.6, 1508.1, 1607.0, 2109.1 (N$_3$ stretch), 2863.5, 2933.0. ESI-MS (CH$_3$OH) $m/z$: 1498.6 (calc. 1498.6 for [ZnM$_3$CH$_3$(ClO$_4$)$_2$]). ESI-MS after demetallation (CH$_3$OH) $m/z$: 1336.5 (calc. 1336.7 pour [M$_3$CH$_3$(ClO$_4$)$_2$]).
Figure S4.37 $^{13}$C NMR (CD$_3$CN, 63 MHz, 300 K) [ZnM$_{3}$OH]ClO$_4$$_2$

Figure S4.38 ESI-MS (positive ionization, CH$_3$OH) of ligand M$_{3}$OH, displaying peaks for [M$_{3}$OH+H]$^+$ (1336.5), [M$_{3}$OH+Na]$^+$ (1358.5), [M$_{3}$OH+2H]$^{2+}$ (668.8) and [M$_{3}$OH+3H]$^{3+}$ (446.2).
White powder, 85%.

$^1$H NMR (250 MHz, CD$_3$CN, 300 K) δ (ppm): 1.28 (s, 18H, tBu), 1.39 (s, 9H, tBu), 3.18 (t, $J = 5.3$ Hz, 1H, OH), 3.52 (m, 6H, ArCH$_3$), 3.62 (s, 6H, OCH$_3$), 3.64 (s, 6H, NCH$_3$), 3.66 (s, 3H, OCH$_3$), 3.73 (s, 3H, NCH$_3$), 4.07 (m, 6H, ArCH$_2$), 4.51 (d, $J = 5.3$ Hz, 2H, CH$_2$OH), 5.02 (s, 4H, ImCH$_2$), 5.06 (s, 2H, ImCH$_2$), 5.79 (s, 2H, HAr$_{N_3}$), 5.87 (s, 2H, HAr$_{N_3}$), 6.24 (s, 2H, HAr$_{tBu}$), 6.88 (d, $J = 1.7$ Hz, 1H, ImH), 6.89 (d, $J = 1.7$ Hz, 2H, ImH), 6.97 (m, 1H, HAr$_{click}$), 7.04 (s, 1H, HAr$_{click}$), 7.16 (d, $J = 2.5$ Hz, 2H, HAr$_{tBu}$), 7.31 (t, $J = 7.6$ Hz, 1H HAr$_{click}$), 7.35 (d, $J = 2.5$ Hz, 4H, HAr$_{tBu}$), 7.4 (m, 4H, ImH + HAr$_{click}$), 7.67 (s, 1H, H$_{tBu}$). $^{13}$C NMR (63 MHz, CD$_3$CN, 300 K) δ (ppm): 31.5, 32.0, 32.1, 61.3, 61.5, 64.5, 65.0, 101.3, 116.6, 117.0, 123.7, 125.3, 127.6, 127.7, 128.1, 128.4, 128.6, 129.9, 130.0, 130.3, 130.5, 132.4, 132.7, 132.8, 133.5, 134.1, 136.4, 137.0, 137.3, 137.4, 138.8, 144.0, 148.3, 149.2, 153.2, 155.5, 155.6, 156.6. IR (ATR) ν (cm$^{-1}$): 758.0, 1001.9, 1105.3, 1186.8, 1201.2, 1241.9, 1290.6, 1362.3, 1476.6, 1503.2, 1597.1, 2110.0, 2962.7. ESI-MS (CH$_3$OH) m/z: 1546.6 (calc. 1546.6 for [ZnM$_{ArCH2OH}$]+[ClO$_4$]). ESI-MS after demetallation (CH$_3$OH) m/z: 1384.7 (calc. 1384.7 pour [M$_{ArCH2OH}$ + H]$^+$).
4.10 $\text{[ZnM}_{\text{p-NO}_2\text{ArC}_4\text{OH}}]\text{(ClO}_4\text{)}_2$

a. Characterization
White powder, 92%.

**$^1$H NMR (500 MHz, CD$_3$CN, 300 K)** \(\delta\) (ppm): 1.34 (s, 18H, tBu), 1.38 (s, 9H, tBu), 1.42 (m, 4H, \(\beta + \gamma\)), 2.71 (t, \(J = 6.4\) Hz, 2H, \(\delta\)), 3.35 (td, \(J = 6.2\) Hz, \(J = 5.1\) Hz, 2H, \(\alpha\)), 3.55 (m, 6H, ArCH$_{ax}$), 3.63 (s, 6H, OCH$_3$), 3.64 (s, 6H, NCH$_3$), 3.67 (s, 3H, OCH$_3$), 3.78 (s, 3H, NCH$_3$), 4.07 (m, 6H, ArCH$_{eq}$), 4.29 (t, \(J = 5.1\) Hz, 1H, OH), 5.05 (s, 4H, ImCH$_2$), 5.09 (s, 2H, ImCH$_2$), 5.81 (s, 2H, HA$_{N3}$), 5.89 (s, 2H, HA$_{N3}$), 6.34 (s, 2H, HA$_{N3}$), 6.90 (s, 1H, ImH), 6.92 (s, 2H, ImH), 7.40 (m, 9H, HAr$_{tBu} +$ ImH), 7.87 (d, \(J = 8.8\) Hz, 2H, HA$_{NO2}$), 8.24 (d, \(J = 8.8\) Hz, 2H, HA$_{NO2}$). **$^{13}$C NMR (63 MHz, CD$_3$CN, 300 K)** \(\delta\) (ppm): 25.6, 31.5, 31.6, 32.1, 32.7, 32.8, 35.4, 35.6, 35.7, 61.4, 61.6, 61.8, 65.1, 116.8, 117.2, 124.1, 125.4, 125.6, 128.0, 128.5, 129.0, 130.3, 130.4, 130.5, 130.6, 132.7, 133.1, 136.2, 136.4, 136.5, 137.1, 137.3, 137.5, 148.4, 149.3, 149.4, 153.4, 155.5, 155.7, 157.2. **IR (ATR) \(\nu\) (cm$^{-1}$):** 749.3, 854.7, 998.3, 1105.3, 1202.0, 1233.8, 1290.6, 1341.8, 1436.5, 1479.4, 1505.7, 1518.0, 1599.6, 2108.4 (N$_3$ stretch), 2957.8. **ESI-MS** (CH$_3$OH) \(m/z\): 1633.6 (calc. 1633.6 for [ZnM$_{pNO2ArC4OH}^+$ClO$_4$]$^+$). **HRMS** after demetallation \(m/z\): 1471.7481 (calc. 1471.7468 pour [M$_{pNO2ArC4OH}^+$H]$^+$).

**Figure S4.41** $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnM$_{pNO2ArC4OH}$(ClO$_4$)$_2$].

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Figure S4.42 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of [ZnM$_p$NO$_2$ArC$_4$OH](ClO$_4$)$_2$. Zoom on the high-field region.

Figure S4.43 $^{13}$C NMR (CD$_3$CN, 63 MHz, 300 K) [ZnM$_p$NO$_2$ArC$_4$OH](ClO$_4$)$_2$. 

Figure 4.44 ESI-MS (positive ionization, CH$_3$OH) of ligand M$_{pNO2ArC4OH}$ displaying peaks for [M$_{pNO2ArC4OH}$+H]$^+$ (1471.5), [M$_{pNO2ArC4OH}$+Na]$^+$ (1493.4), [M$_{pNO2ArC4OH}$+2H]$^{2+}$ (736.3).

b. VT in CD$_3$CN

Fig S4.43 represents the equilibrium of the displacement of the self-coordinated hydroxyl chain by an acetonitrile molecule, with the associated constant $K = [\text{out}] / [\text{in}]$. The relative proportions of the “in” and “out” complexes were determined by integration of the signals for methylenes $\beta$ and $\alpha$ respectively at various temperatures between 270 K and 325 K (Table S4.2). The associated van’t Hoff plot (Fig S4.44) gave the following thermodynamic parameters: $\Delta_rH^\circ = 454.7 \times 8.31 = 3.8$ kJ.mol$^{-1}$ and $\Delta_rS^\circ = 2.588 \times 8.31 = 22$ J.K$^{-1}$.mol$^{-1}$. 
Fig S4.45 Displacement of the self-coordinated hydroxyl chain of \( \text{[ZnM}_p\text{NO}_2\text{ArC}_4\text{OH}]^{2+} \) by MeCN.

Table S4.2 Percentages of the “in” and “out” complexes of \( \text{[ZnM}_p\text{NO}_2\text{ArC}_4\text{OH}]^{2+} \) and associated equilibrium constant at various temperatures.

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<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>292</td>
<td>26</td>
<td>74</td>
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</tr>
<tr>
<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>325</td>
<td>23</td>
<td>77</td>
<td>3.3</td>
</tr>
</tbody>
</table>

\[ \ln K = \frac{-454.74}{T} + 2.588 \]

\[ R^2 = 0.99159 \]

Fig S4.46 van’t Hoff plot associated with the displacement of the self-coordinated hydroxyl chain of \( \text{[ZnM}_p\text{NO}_2\text{ArC}_4\text{OH}]^{2+} \) by MeCN.

c. Complex \( \text{[ZnM}_p\text{NO}_2\text{ArC}_4\text{OH}(\text{PrNH}_2))(\text{ClO}_4)_2} \)
This inclusion complex was obtained by the addition of 2.0 eq of PrNH₂ to a solution of complex
\([\text{ZnM}p\text{NO}_2\text{ArC}_4\text{OH}(\text{PrNH}_2)]^{2+}\) in CD₃CN.

\(^1\text{H NMR (500 MHz, CD}_3\text{CN, 300 K)}\) \(\delta\) (ppm) : -1.04 (t, \(J = 7.6\) Hz, 3H, \(\gamma\)’), -0.92 (q, \(J = 7.6\) Hz, 2H, \(\beta\)’), 0.79 (m, 2H, \(\alpha\)’), 1.35 (s, 18H, tBu), 1.39 (s, 9H, tBu), 1.42 (m, 4H, \(\beta + \gamma\)), 2.77 (t, \(J = 6.4\) Hz, 2H, \(\delta\)), 2.48 (m, 2H, NH₂), 3.36 (t, \(J = 6.2\) Hz, 2H, \(\alpha\)), 3.54 (d, \(J = 15.9\) Hz, 2H, ArCH₉), 3.65 (d, \(J = 15.8\) Hz, 4H, ArCH₉), 3.59 (s, 6H, OCH₃), 3.68 (s, 3H, OCH₃), 3.80 (s, 6H, NCH₃), 3.81 (s, 3H, NCH₃), 4.10 (m, 6H, ArCH₉), 5.33 (s, 6H, ImCH₂), 6.04 (s, 2H, HArN₃), 6.17 (s, 2H, HArN₃), 6.73 (s, 2H, HAr₉), 6.92 (d, \(J = 1.6\) Hz, 1H, ImH), 6.96 (d, \(J = 1.6\) Hz, 2H, ImH), 7.42 (d, \(J = 2.5\) Hz, 2H, HAr₉), 7.44 (s, 2H, HAr₉), 7.46 (d, \(J = 2.5\) Hz, HAr₉), 7.49 (d, \(J = 1.7\) Hz, 1H, ImH), 7.51 (d, \(J = 1.7\) Hz, 2H, ImH), 7.93 (d, \(J = 8.8\) Hz, 2H, HArNO₂), 8.27 (d, \(J = 8.8\) Hz, 2H, HArNO₂).

Figure S4.47 \(^1\text{H NMR (CD}_3\text{CN, 500 MHz, 300 K)}\) of inclusion complex
\([\text{ZnM}p\text{NO}_2\text{ArC}_4\text{OH}(\text{PrNH}_2)]^{2+}\).
5. Competition experiments

5.1 n = 3 vs. n = 4

- Solutions of the aliphatic amines 4-pentyn-1-amine (C₃NH₂) and 5-hexyn-1-amine (C₄NH₂) in CDCl₃ were prepared, each with an internal standard (DMF and ethylene dibromide (EDB), respectively).

The $^1$H NMR spectra of the solutions were taken.

Fig S5.1 $^1$H NMR (CDCl₃, 500 MHz, 300 K) of the solution of 4-pentyn-1-amine (C₃NH₂) and DMF.
Fig S5.2 $^1$H NMR (CDCl$_3$, 500MHz, 300K) of the solution of 5-hexyn-1-amine (C$_4$NH$_2$) and EDB.

Relative integration of the signals of the amine versus a signal of the internal standard (CH$_3$ for DMF, CH$_2$ for EDB) gave the relative proportions of each amine.

$[\text{DBE}]/[\text{C}_4\text{NH}_2] = (4.11/4)/(2.0/2) = 1.03 \pm 0.05$

$[\text{C}_3\text{NH}_2]/[\text{DMF}] = (2.0/2)/(2.27/3) = 1.32 \pm 0.05$

- Competitive complexations

A mixture of precursor complex $[\text{ZnX}_6\text{N}_3]^{2-}$ in CD$_3$CN and each of the two solutions was prepared and the $^1$H NMR spectrum taken.
Fig S5.3 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of the mixture of host guest complexes HG$_4$ and HG$_3$. 
Fig S5.4 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of the mixture of host guest complexes HG$_3$ and HG$_4$. Zoom on the high field region.

The added number of equivalents of each amine was determined by the relative integration of the corresponding internal standard and the total HArN$_3$ signals of the calixarene.

$$[\text{C}_3\text{NH}_2]^\circ/[\text{calix}] = ([\text{C}_3\text{NH}_2]/[\text{DMF}])^\circ \times [\text{DMF}]/[\text{calix}] = 1.32 \times (23.1/3)/(6.0/6) = 10.1 \pm 1.0$$

$$[\text{C}_4\text{NH}_2]^\circ/[\text{calix}] = ([\text{C}_4\text{NH}_2]/[\text{DBE}])^\circ \times [\text{DBE}]/[\text{calix}] = 1/1.03 \times (43.2/4)/(6.0/6) = 10.5 \pm 1.0$$

The ratio of the host guest compounds was measured by integration of the upfield resonances (methylene β and γ):

$$[\text{HG}_4]/[\text{HG}_3] = 1.30/0.71 = 1.83 \pm 0.10$$

The ratio of the free amines after the complexation is then deducted from the initial value:

$$[\text{C}_3\text{NH}_2]/[\text{C}_4\text{NH}_2] = ([\text{C}_3\text{NH}_2]^\circ-[\text{HG}_3]) / ( [\text{C}_4\text{NH}_2] - [\text{HG}_4]) = (10.1 - 0.71/2)/(10.5 - 1.29/2) = 0.99 \pm 0.10$$

From this we deduct:

$$K_4/K_3 = [\text{HG}_4]/[\text{HG}_3] \times [\text{C}_3\text{NH}_2]/[\text{C}_4\text{NH}_2] = 1.81 \pm 0.20$$

* Competitive monoclick

100 µL of this mixture was diluted in toluene (1.5 mL) and heated at 110°C for 2 hours. The solvent was removed under reduced pressure and the resulting solid dried under vacuum.
Fig S5.5 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) spectrum of the mixture of monofunctionalized complexes [ZnM$_{\text{C3NH2}}$]$^{2+}$ and [ZnM$_{\text{C4NH2}}$]$^{2+}$. Zoom on the high field region.

Relative integration of the upfield resonances gave the ratio of the monofunctionalized complexes:

$$\frac{[\text{ZnM}_{\text{C4NH2}}]}{[\text{ZnM}_{\text{C3NH2}}]} = \frac{(2.0/2)}{(0.88/2)} = 2.27 \pm 0.10$$

Assuming that the ratio of the amines remains constant (large excess), the ratio of the rates of the monoclicks remains constant throughout the reaction. This constant equals both the ratio of the monofunctionalized products and the the ratio of initial rates:

Since the rate of the reaction is: $v_n = k_n[HG_n]$

$$\frac{v_4}{v_3} = \frac{k_4}{k_3} \times \frac{[HG_4]}{[HG_3]}$$

From this we deduct:

$$\frac{k_4}{k_3} = \frac{2.27}{(1.83)} = 1.25 \pm 0.20$$

5.2 $n=4$ vs. $n=5$

- In a similar fashion, solutions of 5-hexyn-1-amine (C$_4$NH$_2$) and 5-heptyn-1-amine (C$_5$NH$_2$) in CDCl$_3$ were prepared, each with an internal standard (EDB and DMF, respectively).
Fig S5.6 $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) of the solution of 5-hexyn-1-amine (C$_4$NH$_2$) and EDB.

$[C_4NH_2]/[EDB] = (2.03/2)/(9.14/4) = 0.44 \pm 0.05$
Fig S5.7 $^1$H NMR (CDCl$_3$, 500 MHz, 300 K) of the solution of 6-heptyl-1-amine ($C_5NH_2$) and DMF.

$$[\text{DMF}]/[C_5NH_2] = (3.46/3)/(2.0/2) = 1.15 \pm 0.05$$

- Competitive complexations

These solutions were added to a solution of precursor complex $[\text{ZnX}_6\text{N}_3]^{2+}$ in $\text{CD}_3\text{CN}$. 
Fig S5.8 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of the mixture of host guest complexes HG$_4$ and HG$_5$. 
Fig S5.9 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) of the mixture of host guest complexes HG$_4$ and HG$_5$. Zoom on the high-field region.

$$([\text{C}_5\text{NH}_2]/[\text{calix}])^\circ = (\frac{([\text{C}_5\text{NH}_2]/[\text{DMF}])^\circ}{[\text{DMF}]/[\text{calix}]}) = \frac{1}{1.15} \times \frac{31.4}{6} = 9.1 \pm 1.0$$

$$([\text{C}_4\text{NH}_2]/[\text{calix}])^\circ = (\frac{([\text{C}_4\text{NH}_2]/[\text{DBE}])^\circ}{[\text{DBE}]/[\text{calix}]}) = \frac{1}{0.44} \times \frac{31.1}{6} = 2.75 \pm 0.50$$

$$[\text{HG}_4]/[\text{HG}_5] = 0.70/1.32 = 0.53 \pm 0.05$$

$$[\text{C}_5\text{NH}_2]/[\text{C}_4\text{NH}_2] = (\frac{[\text{C}_5\text{NH}_2]-[\text{HG}_5]}{[\text{C}_4\text{NH}_2]-[\text{HG}_4]}) = \left(\frac{9.1 - 1.32}{2.75 - 0.70}\right) = 3.52 \pm 0.20$$

$$K_d/K_S = [\text{HG}_4]/[\text{HG}_5] \times [\text{C}_5]/[\text{C}_4] = 0.53 \times 3.52 = 1.87 \pm 0.20$$

- Competitive Monoclicks

Fig S5.10 $^1$H NMR (CD$_3$CN, 500 MHz, 300 K) spectrum of the mixture of monofunctionalized complexes [ZnM$_4$]$^{2+}$ and [ZnM$_5$]$^{2+}$. Zoom on the high field region.
\[
\frac{[\text{ZnM}_{\text{C4NH2}}]}{[\text{ZnM}_{\text{C5NH2}}]} = \frac{(2.41/2)}{(2.0/2)} = 1.21 \pm 0.10
\]

\[
\nu_4/\nu_5 = 1.21 = \frac{k_4}{k_5}.\left(\frac{[\text{HG}_4]}{[\text{HG}_5]}\right)
\]

From this we deduct:

\[
k_4/k_5 = 1.21 \times 2.75/1.46 = 2.28 \pm 0.20
\]

5.3 C\text{4NH}_2 vs. \(\rho\text{NO}_2\text{ArC}_4\text{NH}_2\)

- In a similar fashion, solutions of 5-hexyn-1-amine (C\text{4NH}_2) and 6-(4-nitrophenyl)-5-hexyn-1-amine (\(\rho\text{NO}_2\text{ArC}_4\text{NH}_2\)) in CD\text{3CN} were prepared, each with an internal standard (EDB and DMF, respectively).

Fig S5.11 ^1\text{H} NMR (CD\text{3CN}, 250 MHz, 300 K) of the solution of 5-hexyn-1-amine (C\text{4NH}_2) and EDB.

\[
\frac{[\text{C}_4\text{NH}_2]}{[\text{EDB}]} = \frac{(2.00/2)}{(4.33/4)} = 0.92 \pm 0.05
\]
Fig S5.12 $^1$H NMR (CD$_3$CN, 250 MHz, 300 K) of the solution of $p$NO$_2$ArC$_4$NH$_2$ and DMF.

$[\text{DMF}]/[p\text{NO}_2\text{ArC}_4\text{NH}_2] = (9.04/6)/(2.0/2) = 1.51 \pm 0.05$

- Competitive complexations

These solutions were added to a solution of precursor complex $[\text{ZnX}_6\text{N}_3]^{2+}$ in CD$_3$CN.
Fig S5.13 $^1$H NMR (CD$_3$CN, 250 MHz, 300 K) of the mixture of host guest complexes HG$_4$ and HG$_{NO2}$.

Fig S5.14 $^1$H NMR (CD$_3$CN, 250 MHz, 300 K) of the mixture of host guest complexes HG$_4$ and HG$_{NO2}$. Zoom on the high-field region.
\[
([p\text{NO}_2\text{ArC}_4\text{NH}_2]/[\text{calix}])^\circ = ([p\text{NO}_2\text{ArC}_4\text{NH}_2]/[\text{DMF}])^\circ \times [\text{DMF}]/[\text{calix}] = 1/1.51 \times (177/6)/(6.2/6) = 18.8 \pm 1.0
\]

\[
([\text{C}_4\text{NH}_2]/[\text{calix}])^\circ = ([\text{C}_4\text{NH}_2]/[\text{EDB}])^\circ \times [\text{EDB}]/[\text{calix}] = 0.92 \times (33.5/4)/(6.2/6) = 7.42 \pm 0.50
\]

\[
[H_G]/[H_G\text{NO}_2] = 0.76/1.22 = 0.62 \pm 0.05
\]

\[
[p\text{NO}_2\text{ArC}_4\text{NH}_2]/[\text{C}_4\text{NH}_2] = ([p\text{NO}_2\text{ArC}_4\text{NH}_2]^\circ \times [H_G\text{NO}_2]/([\text{C}_4\text{NH}_2]-[H_G])) = (18.8-1.22/2)/(7.42-0.76/2) = 2.58 \pm 0.20
\]

\[
K_d/K_{\text{NO}_2} = [H_G]/[H_G\text{NO}_2] \times [\text{C}_\text{NO}_2]/[\text{C}_4] = 0.62 \times 2.58 = 1.60 \pm 0.20
\]

- Competitive Monoclicks

Fig S5.14 'H NMR (CD$_3$CN, 250 MHz, 300 K) spectrum of the mixture of monofunctionalized complexes [ZnM]$^{2+}$ and [ZnM$_{p\text{NO}_2\text{ArC}_4\text{NH}_2}$]$^{2+}$. Zoom on the high field region.

\[
[ZnM_{\text{C}_4\text{NH}_2}]/[ZnM_{p\text{NO}_2\text{ArC}_4\text{NH}_2}] = 1.26/0.79 = 1.59 \pm 0.10
\]

\[
\nu_4/\nu_{\text{NO}_2} = 1.59 = (k_d/k_{\text{NO}_2}) \times ([H_G]/[H_G\text{NO}_2])
\]

From this we deduct:

\[
k_d/k_{\text{NO}_2} = 1.59/0.62 = 2.60 \pm 0.20
\]
6. Conformational analysis of monofunctionalized complex \([\text{ZnM}_{\text{ArCH2NH2}}]^2+\)

<table>
<thead>
<tr>
<th>([\text{ZnX}_6\text{N}_3]^2+)</th>
<th>CH (_2)</th>
<th>d</th>
<th>a</th>
<th>c</th>
<th>b</th>
<th>(\text{Bu})</th>
<th>OCH (_3)</th>
<th>NCH (_3)</th>
<th>ImCH (_2)</th>
<th>HArN</th>
<th>ImH</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{ZnX}_3\text{N}_3]^2+)</td>
<td>1.38</td>
<td>3.65</td>
<td>3.65</td>
<td>5.04</td>
<td>5.91</td>
<td>6.88</td>
<td></td>
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<tr>
<td>([\text{ZnM}_{\text{ArCH2NH2}}]^2+)</td>
<td>3.86</td>
<td>7.46</td>
<td>7.38</td>
<td>7.29</td>
<td>7.3</td>
<td>1.27 (18H)</td>
<td>3.53 (6H)</td>
<td>3.78 (3H)</td>
<td>5.95 (2H)</td>
<td>6.88 (1H)</td>
<td>6.43 (tria)</td>
</tr>
<tr>
<td>([\text{ZnM}_{\text{ArNH2}}]^2+)</td>
<td>-0.12 (18H)</td>
<td>-0.01 (6H)</td>
<td>-0.03 (6H)</td>
<td>-0.20 (4H)</td>
<td>-0.01 (N(_3))</td>
<td>-0.02 (2H)</td>
<td>0.21 (tria)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(\Delta \delta_{\text{Bu}}\) 0.52 -0.02 0.13 0.35 0.47 0.06 (9H) 0.24 (3H) 0.10 (3H) 0.12 (2H) -0.12 (9H) -0.10 (1H)

Table S6.1. From top line to bottom line: chemical shifts in ppm (CD\(_3\)CN, 300 K) of A) \([\text{ZnX}_6\text{N}_3]^2+\); B) Free amine ArCH2NH2; C) Inclusion complex HG\(_{\text{ArCH2NH2}}\); D) CIS; E) Monofunctionalized product \([\text{ZnM}_{\text{ArCH2NH2}}]^2+\); F) \(\Delta \delta\).

**Orientation of the Ar\(_{\text{tria}}\) unit:**

OCH \(_3\) (3H) resonates at 3.78 ppm, which is very close to the equivalent methoxy in \([\text{ZnM}_{\text{C4NH2}}]^2+\) (3.76 ppm). This indicates that the position of the aromatic unit is very similar in both complexes.

We cannot compare the chemical shifts of the HAr\(_{\text{tria}}\) or H\(_{\text{tria}}\) protons due to the difference in electronic effect of the aromatic guest compared with the aliphatic spacer.

**Orientation of the two ArN\(_3\) units, deviation from the original cone conformation.**

The deviation of the two remaining ArN\(_3\) units can be measured by the average position of their two protons (average of the chemical shifts). In this case, the average chemical shift is 5.95 ppm, which is significantly lower than the 6.17 ppm value for \([\text{ZnM}_{\text{C4NH2}}]^2+\). This upfield shift likely comes from shielding effect of the aromatic guest.

**Twisting of the calixarene**

The twisting of the calixarene can be measured by the splitting of protons. It is greater than the most twisted complex with an aliphatic chain \([\text{ZnM}_{\text{C3NH2}}]^2+\) in every case (\(\text{Bu}: 0.18\) for \([\text{ZnM}_{\text{ArCH2NH2}}]^2+\), 0.09 for \([\text{ZnM}_{\text{C3NH2}}]^2+\); OCH \(_3\): 0.25 for \([\text{ZnM}_{\text{ArCH2NH2}}]^2+\), 0.22 for \([\text{ZnM}_{\text{C3NH2}}]^2+\); ImCH \(_2\): 0.32 for \([\text{ZnM}_{\text{ArCH2NH2}}]^2+\), 0.21 for \([\text{ZnM}_{\text{C3NH2}}]^2+\); HArN \(_3\): 0.55 for \([\text{ZnM}_{\text{ArCH2NH2}}]^2+\), 0.22 for \([\text{ZnM}_{\text{C3NH2}}]^2+\)).

In this complex, the calixarene is more twisted than the one with any of the aliphatic spacer (\([\text{ZnM}_{\text{C3NH2}}]^2+\) is the most twisted of the three with the greatest split of the protons).